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SOFT X-RAY K-ABSORPTION AND EMISSION SPECTRA OF Mg, Al, Si AND THEIR OXIDES

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(Received for publication, December 12, 1946)

ABSTRACT. The K-absorption spectra of Mg, Al, and Si in pure state and in oxides and also their K-emission bands have been taken with a concave crystal (gypsum) spectrograph designed and constructed in Prof. Siegbahn's laboratory. Coincidence of the absorption and emission edges in Al and Mg have been studied accurately in the same film by half shadow device. The absorption edges for oxides are shifted towards short wavelength side with respect to the metal emission bands for the oxides. For the oxides the gap between the beginning of the absorption edge and the short wavelength limit of the emission band is, according to the Zone theory, the forbidden energy gap which has to be correlated with the order of insulation.

INTRODUCTION

The group of papers, of which the present is the first, describes the results of examination of the soft X-ray K-absorption and emission spectra of Mg, Al, Si and their oxides. To interpret the distinctive properties of solid matter in general, *e.g.*, copper (metallic), rocksalt (ionic), carborandum (homo-polar), copper-oxide (semi-conductor) etc. a unified theory based on modern quantum and wavemechanical conceptions have been developed by Brillouin, Bloch, Peirles and others. On the experimental side the soft X-ray spectroscopy of the solid state, investigated by, Siegbahn and Karlson, Skinner and O'Bryan, Magnusson and Johnson, Farineau and others, throws much light on the proposed theory of the solid state.

Soft X-ray absorption spectra give information relating to those states of the solid which in the normal state of the lattice are unoccupied, while the emission bands give information relating to those states of the solid which are normally occupied. A complete study of the zone structure necessitate the investigation both by absorption and emission process. The discrepancies of the experimental data of the soft X-ray spectra for different investigators will at once suggest a thorough study of a particular substance by the same experimenter in the same spectrograph. If possible, the absorption as well as the emission spectra for a particular substance is to be taken on the same photographic film by some half-shadow device.

Considerable work has already been done on the soft X-ray absorption and emission bands. The K-absorption of Mg and Al and $L_{2,3}$ absorption of Mg were investigated by Sandstrom (1935) Skinner and Johnston (1937). Skinner and O'Bryan (1940) have studied the L and M emission bands lying in the range from about 17 to 300A with ruled grating. Although the resolution in the region between 40 to 500A is better compared to the region between 5 to 15A, there is an advantage of studying the K-absorption or

emission bands between 5 to 15A compared to the study of L_{23} bands for the same substances between 40 to 500A. The K-emission bands produced by the transition of valence electrons to the vacant K level will obviously be simpler compared to the L_{23} bands produced by the transition of the same valence electrons to the vacant L_{23} levels which are themselves splitted and for the compounds of low atomic numbers are profoundly modified due to the lattice formation.

EXPERIMENTAL TECHNIQUE

The range of wavelengths for the present invesitgation stretches from about 5A to 12A; this region of spectra being highly absorbable in air the whole spectrograph with crystal, plateholder etc. had to be kept in the same vacuum as the X-ray tube itself The bent crystal method enables us to obtain good photographs of emission bands as well as absorption edges with natural crystals gypsum, mica as grating without a slit the latter being for a long time considered as a necessary implement in the apparatus. The principle of focussing of the spectra is the same as in Rowland's grating. X-ray from anti-cathode passing through a 4 mm aperture forming a divergent beam strike the bent crystal and are focussed to a point on the Rowland's circle. The bent crystal with a portion of the Rowland's circle known as the 'cassette' moves as a whole about an axis passing through the centre of the crystal. The cassette with the crystal holder can be rotated by a pointer from outside without disturbing the vacuum of the spectrograph for suitable angles for different wavelengths. Sandstrom (1935) has calculated the broadening of the spectral line for various causes and has shown that apart from other factors, it increases with the square of the effective reflecting surface of the bent crystal. This defect is generally met with a spectrograph of large radius and small crystal width. In the spectrograph used the Rowland's circle has got a radius of 250 mm and the crystal is bent to an arc of radius 600 mm. Between the two curved steel pieces (500mm radius) is placed a thin slice of a single crystal of gypsum of about 0.5 mm thickness and the bending is effected by screws attached to the steel piece. The reflecting surface of the crystal has been limited by controlling the width of the diverging X-ray beam by an wedge moving at right angles to the crystal surface. In the present investigation the spectrograph was used between glancing angles 20°-50°. The maximum possible broadening as calculated by Sandstrom was found to be ·05 X.U within this range of angles which is of little importance to us as the experimental errors for measuring broad bands are larger than this value. The lattice constant and the refractive index of bent crystal could not be determined directly and the value of the same for the unbent crystal has been used. The change in the spacing value due to bending has been discussed by Sandstrom and the ratio $\Delta d_n / d_n$ where d_n is the spacing of the nth order was found to be practically constant for all orders of reflections. The error due to broadening is in the

fourth place of the '*d*' value and decreases rapidly with the higher orders. In the same paper other possible errors of secondary importance, *e.g.* due to any flaw in the bending of the crystal, due to difference of penetration of the higher order reference lines into the photographic film and the like, have been discussed. These probable errors are always less than the experimental limit. The anti-cathode which is water cooled and the cathode which is a 'dull emitter' consisting of oxide coated platinum wire face each other inside a light-tight enclosure fitted with a slightly tapering cone of about 2 cm. in length and 4 mm aperture to allow X-rays to be admitted to the spectrograph. A thin piece of Al of thickness about 0.5μ is generally used for covering the aperture to protect the film from the glow of the filament. A good oxide coating has been prepared with BaO and SrO taken at a definite proportion and the coating on the filament lasts for about 30 hours.

The dispersion in this region varies from 0.2 to 0.7 volt/mm. It was calculated in every case for the particular region under investigation by taking suitable reference lines. In some cases reference lines of higher orders have to be taken and this generally increased the background radiation to such an extent that finer details of soft X-ray absorption and emission bands were completely lost. In order to avoid this difficulty the film was carefully half covered when the line in question was photographed in the other half. To calculate the wavelength for the higher order spectra the corresponding '*d*' values for the gypsum and wavelengths for reference lines were taken from Siegbahn's 'Spectroscopy der Rontgenstrahlen.'

Preparation of absorption screens: In taking absorption spectra it has been noticed that the suitable thickness and the quality of the absorbing screens are essential for having a good photograph. Based on absorption laws of Jonsson, Sandstrom (1935) derived a formula for calculating the optimum thickness of screens so as to have the maximum difference between the intensity on each side of an edge, but this can be taken as the lower limit of the screen thickness. From experience it has been found that fine structure details come out better if the thickness of the absorbing screen is too small while a greater thickness is necessary to have a prominent primary edge. Films of different samples were made by different suitable processes and therefore it was difficult to determine the actual thickness of the film. Metal films of Mg and Al were prepared by rolling process whereas oxides were coated on a thin film of celluloid.

Aluminium.—Six pieces of Al, each of thickness of about 0.5 μ, gave only a prominent absorption edge, while with three pieces three secondary absorption edges are clearly visible on the film.

Magnesium.—A rod of pure metallic Mg was rolled and the film thickness was found to be too great. This was then scrapped with a fine blade and a fairly uniform film could be made which have a prominent primary edge.

Silicon and Al_2O_3.—Very fine powders of metallic Si preserved in sealed tubes was thoroughly mixed with a large quantity of a solution of celluloid

in acetone and spread over a ground glass. Acetone soon evaporates and the thin film of silicon in celluloid sticking to the glass is removed by adding water and dried in vacuum. The film for Al_2O_3 was also prepared in a similar way.

MgO.—For MgO pure Mg was burnt in air and MgO smoke was allowed to deposit on an Al foil of thickness 0.5 μ.

Photographic film.—Single coated Agfa Laue film used by workers in this region was not available in the market due to war censor. Fine grain cinema films used for sound track photography was found suitable for the purpose. The grains are remarkably fine for good microphotometer work though the speed is much less than that of the sensitised Laue films.

GENERAL INTERPRETATION OF RESULTS

According to the theory of solids, all the energy levels of an atom, particularly the valency ones, are greatly modified by the interaction of neighbouring atoms in the lattice and as a result these levels become broad. The broad valency levels may sometime overlap with the next possible higher one. The combined level thus formed is now filled up with electrons according to Pauli-principle up to a certain limit and the rest is empty. This limit which demarcates the two portions of the combined level is known as Fermi-surface which is very sharp at ordinary temperature and is usually denoted by energy maximum E_{max}. The beginning of the band is, however, represented by E_o. It is evident that the intensity of any emission line, corresponding to transition of electrons from the valency shell to a deeper vacant level, will suddenly vanish at E_{max} where the absorption edge of the atom in the crystal will just begin. The theory of solid metal correctly interprets the general experimental observations on both the emission and absorption spectra in the soft X-ray region. Further, it is found that the emission edges of the elemement of the second group of metals in the L series are very sharp and are of the order of 1/10 e.v. suggesting the sharpness of the Fermi-surface, whereas the same surface as measured from K-emission spectra for those elements varies from 2 to 4 volts. It has been pointed out by Ray and Bhowmik (1941) that the K-emission edge is partly modified by the absorption of general radiation by the inner surface of the anticathode and has been verified by the author in the case of Mg and Al by taking emission band at high and low voltage of excitation.

K-valence emission band of Mg, Al and Si and the absorption edges of these elements were studied under similar conditions that is the effective surface of the reflecting crystal, the aperture of the incident radiation, the slit system of the micro-photometer were kept constant. In the curves Fig. 2(*a*), (*b*), (*c*) maximum blackness on the plate, *i.e.*, peak of the emission band I_{max} of all the spectra was taken as a standard at a definite length and corresponding points on the emission lines were necessarily altered in the

same ratio. In the absorption spectra the maximum difference in blackness before and after the absorption was similarly taken at the same length as in emission curve. The other points were then plotted as before. The abscissa is drawn on the voltage scale. It will not be out of place to mention here that I_{max} in the intensity curve is necessarily different from E_{max}, the latter depends on the energy value of the Fermi-surface of the combined level whereas the former is related by the following equation : $I=N(E).f(E)$, where N(E) denotes the density of states and $f(E)$ the transition probability. Thus intensity will be maximum when $N(E).f(E)$ is maximum and it will be zero just after E_{max} where there are no electrons.

In the emission process an electron is knocked out from inner shell into the vacancy, transition of an electron from the continuous band of filled valence levels may occur. This gives accurately the characteristics of the N(E) curve over the region of filled levels. Before the emission process the lattice has all its normally occupied states filled except that there is a vacancy in the inner shell. The energy of the initial state is therefore sharply defined within the limits of the breadth of the inner level. After the emission an electron may be missing from any of the levels of the filled valence electron band. While in the case of absorption we are simply concerned with the probability of transition from the inner level into one of the vacant levels. The characteristics of the N(E) curve for the vacant levels will obviously be reflected in this absorption curve.

The photometer records of absorption spectra for Mg, Al, Si and their oxides are given in Fig 1. The point of interest in the experiment was to

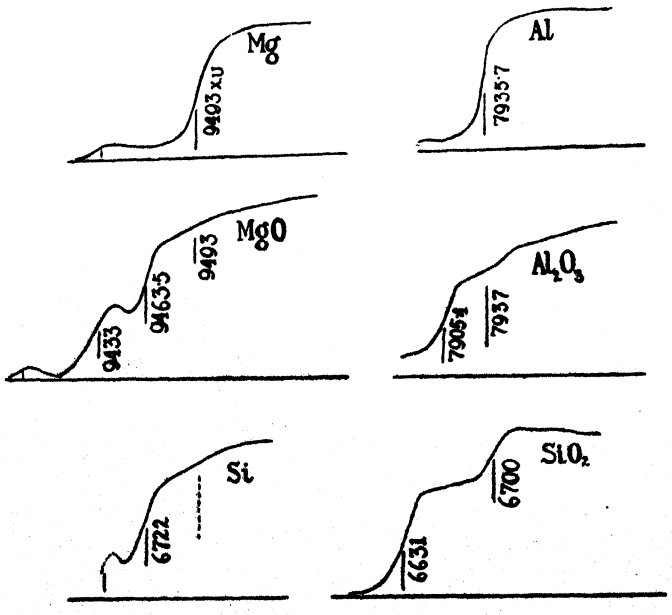

FIG. 1

Photometer records of K-absorption spectra of Mg, Al, Si and their oxides, wavelengths in X.v.

investigate the exact position in the wavelength scale of the beginning of K—absorption edge of Mg, Al, and Si and to compare this with the short wavelength limit of the emission edge E_{max}. In the first set of experiments the emission and absorption photographs were taken in different photographic films and it was really two different settings of the spectrograph. In order to have a more decisive result, the crystal angle was kept same in both emission and absorption experiments, and the lower-half of the photographic film bent round the Rowland's circle (cassette) was first covered by a rectangular strip of metal and emission band was taken on the upper part of the film. In the next set of absorption experiment, the upper portion was covered similarly and the absorption edge was recorded in the lower portion of the *same film*. This was necessary because a slight variation of pressure over the film could alter the position of the film relative to the Rowland's circle. In this way we got on the same film both K-absorption edge and K-β emission band of Mg, Al, and Si under the same condition.

The film was then etched by a fine blade so that the scratch is parallel to the sharp emission lines which are also present along with emission bands. The scratch, the emission lines and the absorption edges were all made parallel to the vertical slit of the micro-photometer.

First the photometer record of the emission band was taken along with the scratch which was recorded as a sharp peak, then the absorption edge was taken by lowering or raising the film by a simple mechanism without disturbing the film and this time also the fine scratch of blade on the film gives a peak. Now it was seen that the position of the peaks, *i.e.*, fine scratch does not alter in the two cases showing thereby that there is no lateral movement of the film when it is simply raised or lowered.

From several such experiments it was found that decidedly there is no lateral shift in the two sets of photometer records, *i.e.*, on the bromide paper on which record is taken the peaks for the fine scratch come on the same position. The micro-photometer record thus consists of superposed emission and apsorption spectra, the dispersion and magnification for the two being the same. From the superposed spectra it is evident that absorption begins definitely at a longer wavelength than the wavelength corresponding to the most intense (I_{max}) part, *i.e.*, peak of the emission band and at a still more longer wavelength than the wavelength corresponding to E_{max} of the emission band. The experiment was repeated several times.

Beginning from the long wavelength side we have marked three important positions of the emission band. First 'E_0' Fig. 2(*a*) which corresponds to the beginning of the band on the longest wavelength side, *i.e.*, X-ray produced by the transition of electrons from the bottom of the filled conduction band to the inner shell. The second point marked, is named as I_{max} corresponding to intense peak of emission band, *i.e.*, when $N(E) \times f(E)$ is maximum. The third point marked in the emission band is E_{max} corresponding to the shortest wavelength of the emission band, *i.e.*, according to the theory

corresponding to the transitions of electrons from the Fermi-surface to the inner shell.

In the absorption spectra we have also marked the three points *viz.*, the beginning B and end L of the absorption curve and middle portion K where usually primary edge K is measured. Absorption begins at the longest wavelength corresponding to the energy required to transfer a K-electron to the bottom of the empty zone or just after the Fermi-surface where there is no electron. The K-absorption edge and K-valence emission band taken carefully on the same film clearly show that absorption begins at a much longer wavelength than I_{max} of the emission band in the case of Mg, Al, and Si.

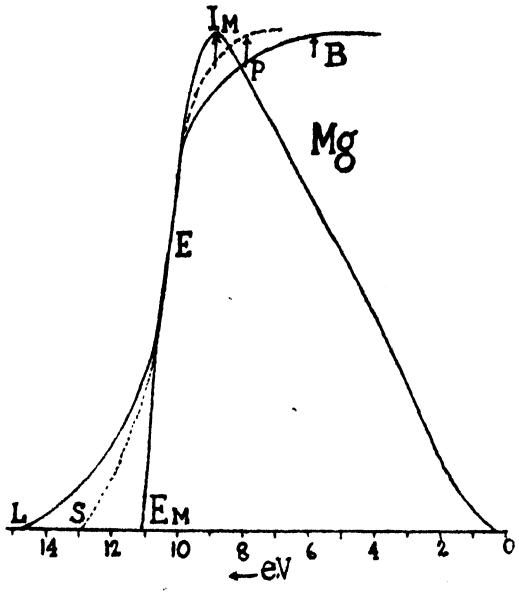

FIG. 2(*a*)

I_M is the peak of the K-emission band of Mg and B is the beginning of K-absorption for short period exposure and P is the same for long exposure. L is the end of absorption curve for long exposure and S the same for short exposure. E_M is the short wavelength limit of the emission band. The point P is one volt from I_M on the low energy side. E is emission edge coincident with absorption edge.

Magnesium and Aluminium.—The absorption curves for magnesium and aluminium are given in Fig. 1, in magnesium one secondary edge and in aluminium three prominent secondary edges have been obtained. The breadth $I_M - E_M$ in Mg emission band is 2 volts and in Al it is 4.5 volts Fig. 2(*a*) and 2(*b*). The position of E_{max} that is, E_M in the figure is, however, uncertain as it depends on the time of exposure and this has been shown to be due to the absorption of general radiation by the inner surface of the anti-cathode and can be sometimes avoided by taking emission band at a low exciting voltage of the tube. The dotted and continuous lines near the end of the absorption curve are found to occur under short and long exposures

respectively. The difference between them for Mg is 1.8 volt. Altogether five absorption photographs were taken both for Mg and Al, having different time of exposures and it has been found that the beginning of the absorption B, *i.e.*, the bending of the absorption curve also shifts towards the short

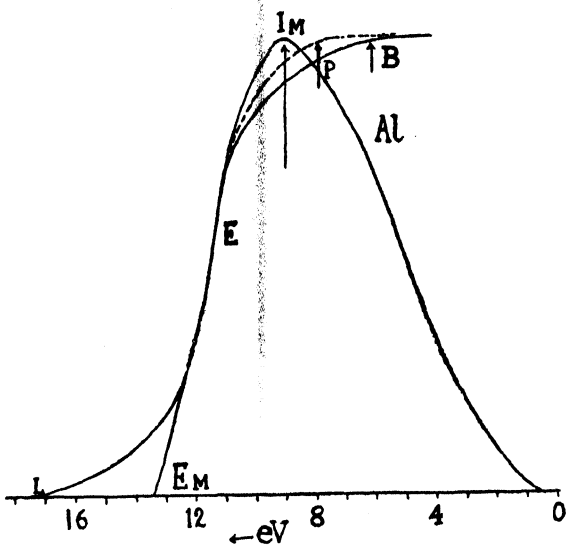

FIG. 2(*b*)

I_M is the peak of the K-emission band of Al and B is the beginning of K-absorption for short period exposure and P the same for long exposure. E_M is the short wavelength limit of the emission band. L is the end of the absorption curve. The point P is about 1 volt from I_M on the low energy side. E is emission edge coincident with absorption edge.

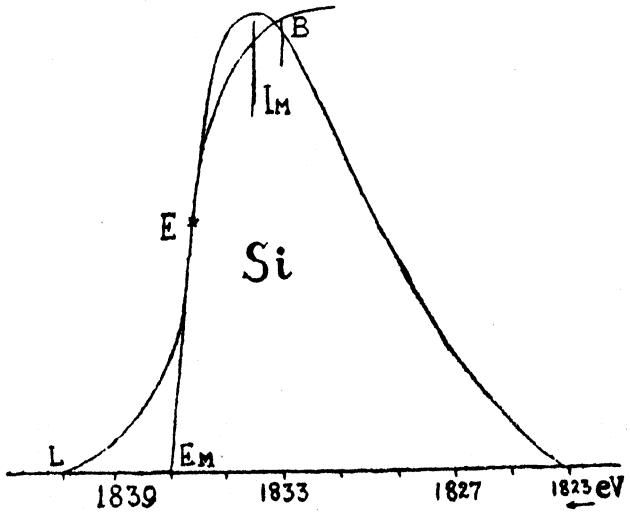

FIG. 2(*c*)

I_M is the peak of K-emission band of Si and B the beginning of K-absorption. E_M is the short wave limit of the emission band and L the end of the absorption curve. The point B is about one volt from I_M on the low energy side. E is the emission edge coincident with the absorption edge.

wavelength side with prolonged exposure. This is shown in Fig. 2(*a*), 2(*b*). The photometer record of Mg emission band superimposed on Mg absorption curve taken on the same film by half-shadow device and the same for Al is given in Fig. 3. From repeated experiments it is seen that absorption begins at least one volt before I_M, the peak of the emission band, on the long wavelength side, both in the case of Mg and Al.

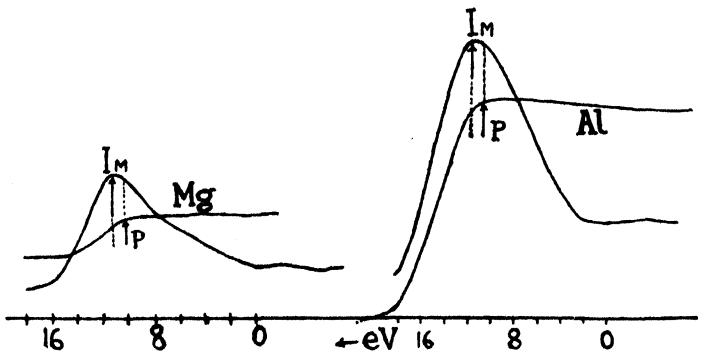

FIG. 3

Micro-photometer record of absorption and emission curves taken in the same film by half-shadow device. I_M is the peak of the emission band and P is the beginning of absorption.

According to the solid theory of the metals the combined level is filled up with necessary electrons according to Pauli-principle, an electron from the K shell cannot find any place within the limit E_0 to E_M. The experiment shows that absorption surely begins before E_M, in other words the total number of *p*-electrons allowed by Pauli-principle which are responsible for K-emission band is not actually present in the combined portion of s, p zones of Mg in the solid, at least under the experimental condition The absorption experiment shows that '*p*'-electrons can be accomodated in the '*p*'-band even within the overlapping portion of 's,' 'p' zones, but the number of such *p*-electrons is found to be small (as estimated from absorption intensity) inside the deepest *p*-level and it gradually increases till E_M is reached, just after which the absorption becomes maximum. It is interesting to note that Skinner (1940), from observations of the kinks in L_{23} bands, suggests that an overlapping between 's', 'p' zones in Mg solid is of the order of 2 volts. According to us it is of the order of 3 volts or more.

The total width of the *p* level in the crystal where K electrons can be accomodated, as measured from the K-absorption edge (including the overlapping position) in Mg solid, is 9 volts and 7 volts for long and short exposures respectively. It is found that the middle portion of the absorption edge coincides with that of the emission edge. The suggestion which has been made in Mg spectra may also be applied in the case of Al. Skinner finds that the overlapping of 's', 'p' zones from L_{23} band spectra is of

the order of 3 to 4 volts in the case of Al and according to our absorption result in Al the overlapping is of the same order, *i.e.*, 3 to 4 volts. The total breadth of the 'p' band from absorption edge is 9 volts and 11 volts for short and long exposures.

Silicon —In the case of Si metal K-emission band is always associated with a weak K band of Si in SiO_2. The peak of K band of metal is at 6731 X.U. and of SiO_2 is 6746 X.U. The empirical band width of Si metal is 14 volts. Uncertainty for the position of E_M is introduced, as in the case of Mg and Al, due to anti-cathode absorption and on the long wavelength side due to superposition with K band of Si in SiO_2, the long wave limit is difficult to be determined.

In the absorption spectra of Si metal there seems to be on the longer wavelength side a faint edge and it is difficult to find out the position of the edge (see Fig 1). In Fig. 2(*c*) the K-emission band of Si metal is drawn on the same scale, as stated previously along with the prominent primary K-absorption edge. As in the case of Mg and Al the middle portion of both emission and absorption edge do coincide, marked E in the Fig. 2(*c*). The absorption, however, begins one volt before I_M, the peak of the emission band.

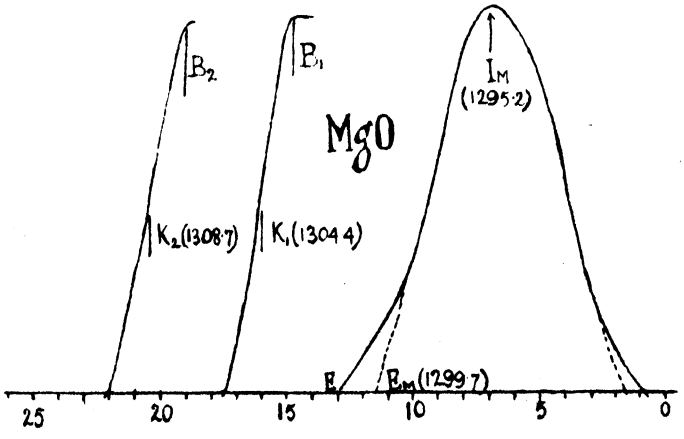

FIG. 4(*a*)

I_M is the peak of K-emission band of MgO and E_M is the empirical short wave limit of emission band, neglecting the weak band at short wavelength end. B_1 and B_2 are the beginning of primary and secondary edges respectively.

Magnesium Oxide.—The absorption curve photometer record is shown in Fig. 1. The edge Mg in MgO shifts towards the short wavelength side with respect to K edge of metallic Mg and absorption begins at a shorter wavelength than emission end E_M. The difference between the K-absorption edge and I_M the peak of the emission band is 9 volts Fig. 4(*a*). An ultra-violet absorption band of this order is to be expected for MgO. The difference

between the beginning of K-absorption and E_M is the width of the forbidden zone and is equal to 3.4 volts. This value is unreliable due to uncertainty in the position of E_M caused by the presence of a weak band at the short wave end of the main band. A faint edge due to metal is present in MgO absorption spectra.

Aluminium Oxide.—In Al_2O_3 Fig. 4(*b*) the gap K edge I_M is 12.4 volts, an ultra-violet absorption band of this order is expected. The forbidden energy gap B-E_M is 4.2 volts. A faint edge due to metal is present in the spectra of Al_2O_3 as in the case of MgO. A weak secondary edge has been obtained which is too weak to be accurately determined.

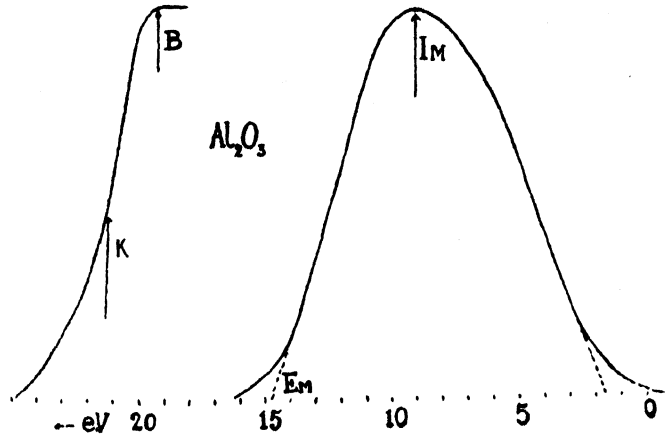

FIG. 4(*b*)

I_M is the peak of the K-emission band Al in Al_2O_3 and B is the beginning of K-absorption. Reduced emission band width is equal to the total K band width of oxygen in Al_2O_3 (Skinner) Fig. 5. The width of the forbidden zone measured from E_M is about 4.7 volts.

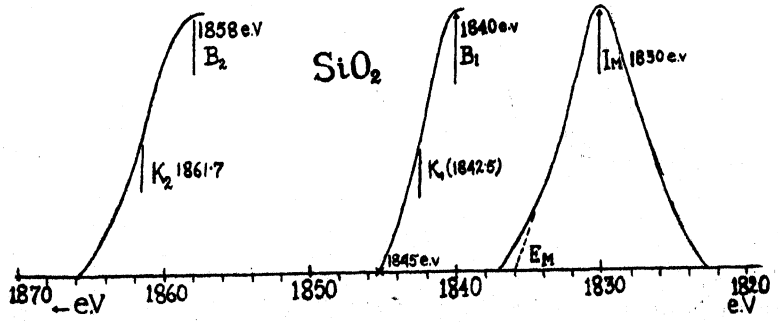

FIG. 4(*c*)

K_1 and K_2 are two absorption edges of Si in SiO_2. Edge K_2 is more prominent. I_M the peak of K-emission band of Si in SiO_2. B_1 and B_2 are the starting point of the two edges. E_M dotted signifying uncertainty of position

Silicon Dioxide.—Two prominent absorption edges have been obtained in the case of SiO_2. Both edges are shifted towards the shorter wavelength

side compared to the edge of metallic silicon. In Fig. 4(*c*) the oxide edges along with the emission band of Si in SiO_2 are drawn on the same scale. The first absorption edge K_1 is less prominent than the second edge K_2. The energy difference between the peak I_M of the emission band of Si in SiO_2 with edges K_1 and K_2 of SiO_2 are 12.5 and 31.7 volts respectively. The forbidden energy gaps B_1-E_M and B_2-E_M are 4 volts and 28 volts respectively.

For various polar and semi-polar compounds the difference K-I_M has been found to agree well with the ultra-violet absorption bands and will be discussed in another paper. The difference B-E_M is a measure of the order of insulation of the material. The total breadth of the absorption edge in oxide is always lower than the corresponding value in metal while in emission spectra they are found to be of the same order of magnitude. Secondary edges are more prominent in oxide compared to those obtained in the case of metals.

(In electron volts)	Mg.	MgO	Al	Al_2O_3	Si	SiO_2
Total breadth of absorption edges:	7.0	3.0	9.0	5.5	8.0	5(Edge K_1) 8(Edge K_2)
Total breadth of emission bands:	11.0	12.0 *10.0	12.8	16.0 *13.0	14.0	14.0 *13.0
Absorption edge-Emission peak:	1.2	9.2(K_1-I_M) 13.5(K_2-I_M)	2.4	12.8 ...	2.0	12.5(K_1-I_M) 31.7(K_2-I_M)
Beginning of absorption—short wave limit of emission band. B-E_M		3.4(B_1-E_M) 7.7(B_2-E_M)		4.2		4.0(B_1-E_M) 28.0(B_2-E_M)

* Reduced empirical width after Skinner.

The K band width of oxygen in various oxides taken by O'Bryan and Skinner (*loc. cit.*) is greater for semi-polar compounds MgO, Al_2O_3, SiO_2, B_2O_5 etc. and less in the case of more polar crystals *e.g.* Li_2O.

The width of valence emission band depends on the amount of overlapping of zones. In a compound of R^+, X^- type there may be three types of overlapping; between R^+ and R^+, X^- and X^- and between R^+ and X^-. Overlapping between R^+ and R^+ and X^- and X^- depends on the ratio of the ionic diameters R^+/X^-. If the size of the negative ion is large compared to that of the positive ion then X^-, X^- overlapping will be predominant and *vice versa*. The amount of broadening due to overlapping of R^+ and X^- will of course be prominent according to the degree of polarity of the crystal. In oxides if a K electron of oxygen is knocked out the vacancy may be filled up by the transition of electron from the valency band, whether it is attached to the positive centre or negative centre. Thus an electron attached to positive ion can fill up the vacancy of the K shell of negative ion and similarly a vacancy of K shell of positive ion may be filled up by the transition of electrones round the negative ion. The above suggestion implies that the K band width of oxygen

in an oxide should be equal to the K band width of metal ion in the same oxide.

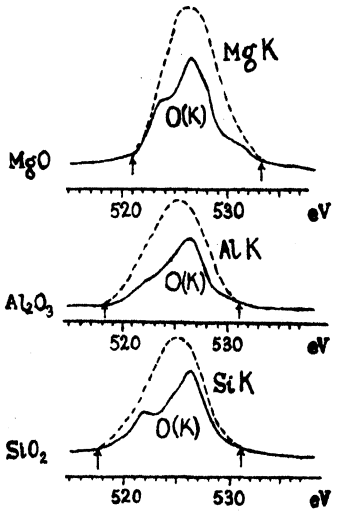

FIG. 5

Photometer records of K bands of oxygen from MgO, Al_2O_3 and SiO_2 O'Bryad and Skinner (1940). Dotted line curves are K metal emission bands of oxides drawn on the same scale.

Our experimental data on the total K band width of Mg, Al and Si in their oxides agree with the K band width of oxygen obtained by Skinner. In Fig. 5, oxygen K band for MgO, Al_2O_3, SiO_2 are drawn on the same scale along with the metal K band. Of course much uncertainty is introduced due to the presence of weak bands at both ends, as well as, due to the tailing effect. In a separate paper the total band width of constituent elements of compounds which are polar, semi-polar and homo-polar will be discussed in detail.

ACKNOWLEDGMENT

I take this opportunity of expressing my gratefulness to the Late Prof. B. B. Ray, University College of Science, Calcutta, under whom the work was done. I am greatful to Prof. S. N. Bose, University College of Science, Calcutta, under whose guidance I am continuing my work on problems of alloys by soft X-ray spectroscopy.

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